# A NEW APPROACH IN DEACTIVATION ANALYSIS: EFFECTS OF COKE LOADING ON DIFFUSIVITY AND ACIDIC PROPERTIES

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## INTRODUCTION

Catalyst deactivation is an inevitable phenomena in any solid catalyst reactions. Numerous studies have been carried out to analyze the kinetics of deactivation due mainly to coke deposition. However, there have been divergent approaches in analyzing this important phenomena.

The kinetics of the main reaction in the presence of coke deposition is generally expressed in a separable form as

$$(-r_A) = (-r_A)_0 \cdot a \qquad (1)$$

where $a$ is the activity as defined by Szepe and Levenspiel [1] or the deactivation function as proposed by Froment and Bishoff [2].

The point of significant differences began in the attempts to define $a$. Froment and co-workers [3-5] strongly argued that $a$ is only a function of the coke content, $a = f(C_C)$. The relationship is determined empirically after several trials. They also use a different deactivation function, $a_C$ for the continuity equation for coke on the catalyst.

On the other hand, Szepe and Levenspiel [1] and Wojciechowski [6] proposed that $a$ is more appropriately related to the reaction time-on-stream, $a = f(t)$. Since then on, researchers on the kinetics of catalyst deactivation are obliged to chose either one of the two approaches.

In this paper we propose a new method that combine both approaches. We begin by redefining eqn 1. Though it has been widely accepted, eqn 1 poses technical difficulties that often lead to large errors. The usage of eq 1 necessitates the need to find expression for the kinetics of the main reaction in the absence of coke, $(-r_A)_0$. The normal procedure is to graphically extrapolate normal kinetic runs to zero time. This practice is bound to introduce large errors in the obtained expression of $(-r_A)_0$.

Another approach is by conducting experiments at very short time-on-stream (pulse feeding method) by assuming that catalyst deactivation is not yet severe. However, there have been no practical guidelines as to how short is the time-on-stream, how little is the amount of feed, and what type of reactions and catalysts that would not result in severe coking. Furthermore, a very short time-on-stream may mean that either thermal cracking was dominat or the reaction was only occuring on the outer surface area of the catalyst.

Catalyst activity is also defined as the amount of active sites that are still available for the main reaction, *ie* sites that are still free from being deactivated by coke deposition. As the reaction time-on-stream increases, the amount of free active sites decreases and the amount of coke increases. Hence, both claims that catalyst activity is related to time-on-stream as well as to the amount of coke are perfectly correct.

The effects of amount of coke and time-on-stream on the activity can be related directly to the rate constants of the main reactions. As will be shown later, this can be easily done by finding the relationship between amount of coke and amount of free active sites, and in turn, between the rate constants of main reaction and amount of free active sites.

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The different amount of coke on the catalyst was obtained by varying the time-on-stream of the reaction. The rate constants of the reaction can be obtained by running kinetic runs at any constant time-on-stream. Since activity can be related directly to the rate constants of the main reaction, there is no need to define activity in a separate term.

Intraparticle diffusivity, $D_i$, is another important parameter in the kinetics of deactivation. However, the values of $D_i$ are often assumed to be constant or are calculated using Knudsen diffusivity. To the best of our knowledge, $D_i$ has never been related to the amount of coke in the catalyst in analyzing the kinetics of deactivation. Masuda, et al. [7] have shown that diffusivity of various hydrocarbons are strongly effected by the amount of coke, especially for zeolite catalysts.

The objectives of this paper are: 1) to correlate the coke amount and acidic properties of the coked catalyst to the rate constants of the main reaction, and 2) to propose a method to predict diffusivity coefficients of large hydrocarbon compounds on coked catalysts.

The reaction system was the catalytic cracking of heavy oil from waste plastics over REY zeolite catalyst [8-10]. The rate constants were obtained from the kinetic run that were performed at a constant time-on-stream of 3h [10].

## MODEL FOR DECREASE IN DIFFUSIVITY

The measurement of diffusivity coefficient of the heavy oil and gasoline components could not be achieved using ordinary volumetric method [11]. This is due to the high vapor pressure of the adsorbate leading to its condensation in the equipment. For this reason, an appropriate model of the diffusivity coefficient was proposed as shown below [11].

$$D = D_0 \exp(-E_0/RT) \tag{2}$$

$$D_0 = (S^2/6)k_{d0}P/(1-P)\exp(\alpha E_d) \tag{3}$$

where

$$P = \frac{3r_0^2}{2R_0^2}\,\frac{\theta_c}{\pi/2} \tag{4}$$

$R_0$ and $r_0$ are radius of the supercage and that of the window of fresh catalyst, respectively. $E_d$, $E_0$, S, a and $k_{d0}$ are parameters and their values have been obtained for several types of hydrocarbons [11].

Assuming coke particles were deposited in supercages and were sphere in shape, $R_0$ and $r_0$ were decreased to R and r, respectively, and were found to have a relationship as follows:

$$r = \frac{R + R_0}{2\sqrt{2}} - \frac{R_0 - R}{2} \tag{5}$$

The relationship between R and the amount of coke loading was obtained experimentally.

## EXPERIMENTAL

### Coke loading

Y-type zeolite which has been deactivated by sintering in steam atmosphere was used for the coke loading experiment. Due to the present of rare-earth metals, REY could not be totally deactivated by steam sintering. The pore sizes of the two zeolites are relatively the same, therefore it is considered that H-type zeolite can be used to substitute REY. Details of the experiment were similar to previous studies [8-10]. By varying the reaction time, catalysts with different amount of coke loading were prepared.

### Measurement of diffusivity

Diffusivities of fresh and coked catalysts were directly measured by a conventional constant volume method [11]. The measurement was performed using n-hexane as absorbent at temperature range of 323 - 423 K and pressure of 1, 3, and 5 torr.

### Measurement of acidic properties

The acidic properties of catalysts were measured by the TPD and TGA experiments..The total amount of desorbed ammonia was regarded as the total amount of acid sites. The amount of that above 573 K was used as the amount of acid sites with strong acid strength [12].

## RESULTS AND DISCUSSION

### Diffusivity

The radii of supercages of coke catalysts, R, were calculated from the diffusivities using eqs 2 to 5. When coke particles were deposited on the surface of the supercages, the value of $(R_o\text{-}R)^3$ should be proportional to the amount of coke. Figure 1 shows the linear relationship between the value of $(R_o\text{-}R)^3$ and the amount of coke loading. Substituting this relation into eq 5, the diffusivity coefficient of coked catalyst can be estimated from the coke amount.

### Relationship between amount of coke loading and amount strong acid sites

The logarithmic value of the amount of strong acid sites were found to decrease proportionally with the amount of coke loading, as shown in Fig. 2. Also, the rate constants were proportinal to the amount of strong acid sites. Combining these relationships, the rate constants of the coke catalysts were expressed in terms of the amount of coke loading, as follows:

$$k_n = k_{on} \exp [-0.136\ W_c] \quad (n = 1 - 5) \qquad (6)$$

The validities of the propose new approach in analyzing the deactivation phenomena are examined by Songip, et al [13]. They have solved the continuity equations of the packed bed reactor which incorporate the dependencies of diffusivity and rate constants on the amount of coke.

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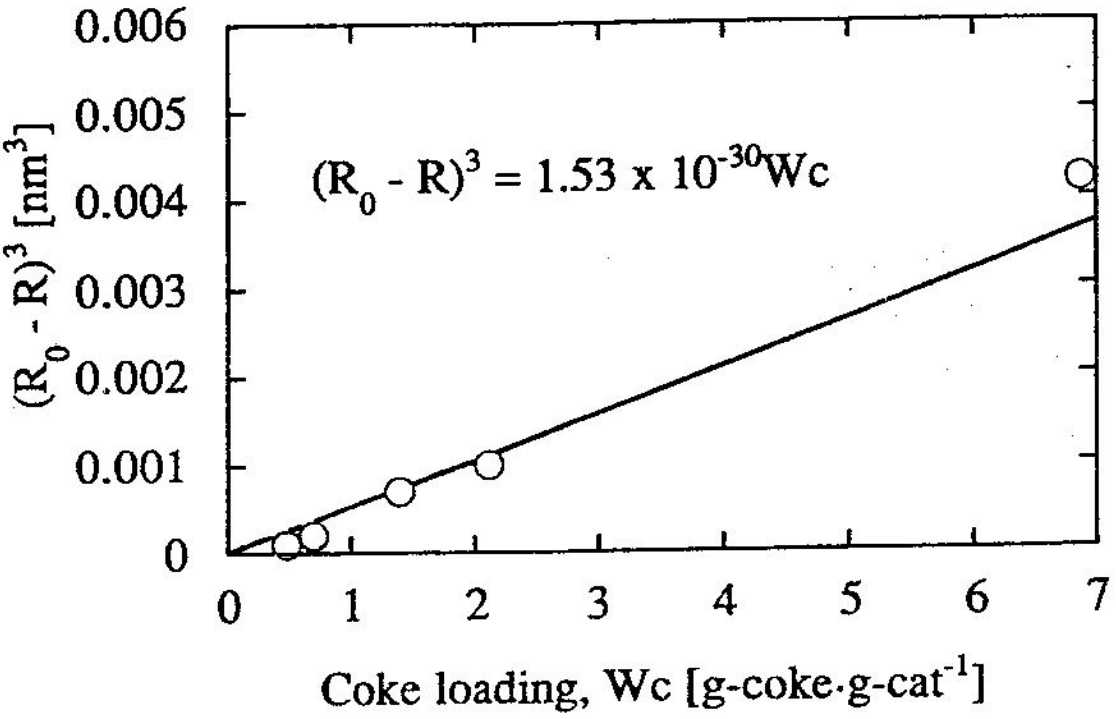


**Figure 1.** Relationship between coke loading and radius of supercages.

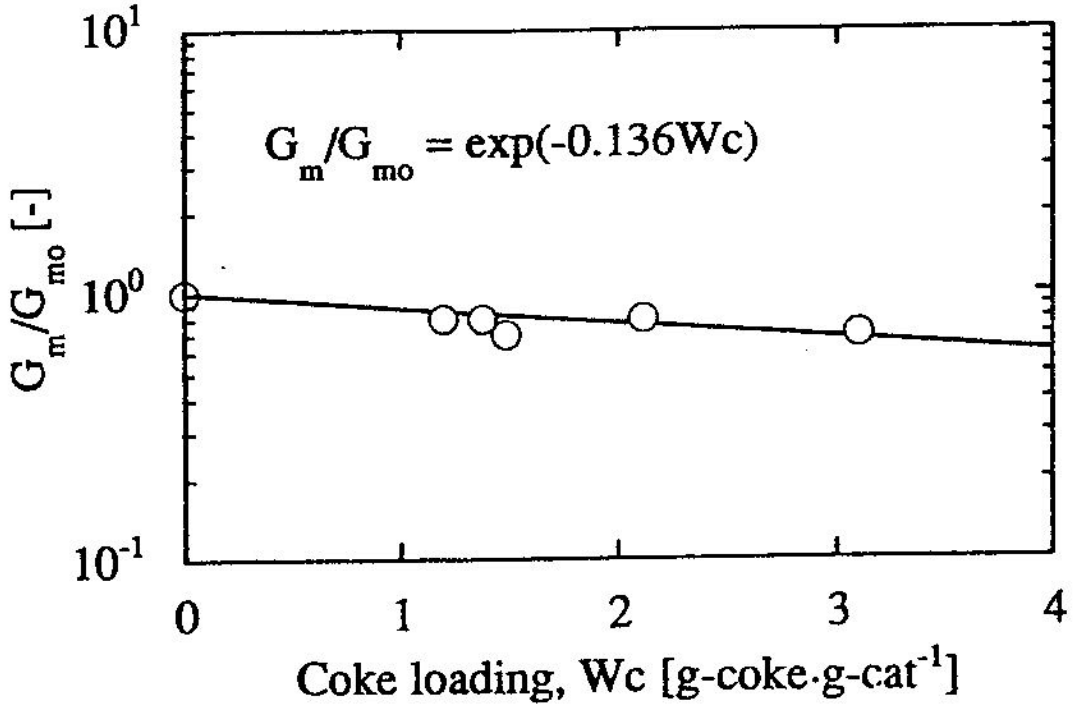


**Figure 2.** Relationship between coke loading and amount of strong acid sites.